Quantum chemistry based methods of modeling of clusters and their applications to the problems of gasdynamics

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Abstract. Different methods of calculation of clusters are concerned from thequantum chemistry point of view. Results obtained with the help of these methods for carbon, water sulfur,alkane are discussed. On the base of this discussion it is made an effort to classify the gasdynamics problems in which clusters play role and to propose the proper quantum chemistry method for each class of problems.

INTRODUCTION

The most important data needed for gas dynamics that could be gained with the help of quantum chemistry is the information about vibration and rotational energy levels as well as the depth of potential energy well. In our investigations we have used a number of different methods which can be in general classified into three brunches. These are:

i) ab-initio
ii) semi-empirical
iii) empirical potential methods.

AB-INITIO METHOD

Ab-initio method is the most precise but most computer power and time consuming. Hence usually it is used for simulating relatively small systems but with high resolution of energy levels and deep elaboration of potential surfaces.

In the reaction of H_2SO_4 formation from SO_3 were found new channels of formation of sulfuric acid, providing that there are water dimers available. There was discovered a new transition state (1), involving two water molecules and SO_3 molecule, having much smaller energy than transition state with only one water molecule (2):

$$SO_3 + (H_2O)_2 \rightarrow H_2SO_4 \circ H_2O \rightarrow H_2SO_4 + H_2O \quad (1)$$

Were checked four possible channels leading to the formation of the sulfuric acid (see the Figure 1):

$$SO_3 + H_2O \rightarrow SO_3 \bullet H_2O \rightarrow H_2SO_4 \quad (2)$$

$$SO_3 + (H_2O)_2 \rightarrow H_2SO_4 \bullet H_2O \quad (3)$$

$$SO_3 \bullet H_2O + H_2O \rightarrow H_2SO_4 \bullet H_2O \quad (4)$$

$$SO_3 \bullet (H_2O)_2 \rightarrow H_2SO_4 \bullet H_2O \quad (5)$$

CP585, *Rarefied Gas Dynamics: 22nd International Symposium*, edited by T. J. Bartel and M. A. Gallis

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (FROM - TO)
09-07-2000	Conference Proceedings	09-07-2000 to 14-07-2000

4. TITLE AND SUBTITLE
Quantum chemistry based methods of modeling of clusters and their applications to the problems of gasdynamics
Unclassified

5a. CONTRACT NUMBER
5b. GRANT NUMBER
5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Plekhanov, E. A. ;

5d. PROJECT NUMBER
5e. TASK NUMBER
5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME AND ADDRESS
International School for Advanced Study
Via Beirut 4
34013 Trieste, Italyxxxxx

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME AND ADDRESS
AOARD
Unit 45002
APO AP, 96337-5002

10. SPONSOR/MONITOR'S ACRONYM(S)
11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
APUBLIC RELEASE
,

13. SUPPLEMENTARY NOTES
See Also ADM001341, Rarefied Gas Dynamics (RGD) 22nd International Symposium held in Sydney, Australia, 9-14 July 2000.

14. ABSTRACT
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15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	Public Release	6	Fenster, Lynn lfenster@dtic.mil
Unclassified	Unclassified	Unclassified			19b. TELEPHONE NUMBER International Area Code Area Code Telephone Number 703767-9007 DSN 427-9007

with these reactions having activation barriers, shown in the Table. 1.
This set of reactions was first treated by Morokuma and Muguruma [1] and recently repeated by us [2]. Thus the most efficiently the formation of sulfuric acid would proceed with the help of reaction (3), which assumes that we have as the initial reagents water dimers and SO_3.

TABLE 1 Activation Barriers for reaction (2-5)				
Reaction	(2)	(3)	(4)	(5)
Energy, Kcal/Mole	32.2	0.7	5.3	12.4

All the calculations were made with the help of the program GAMESS [3].

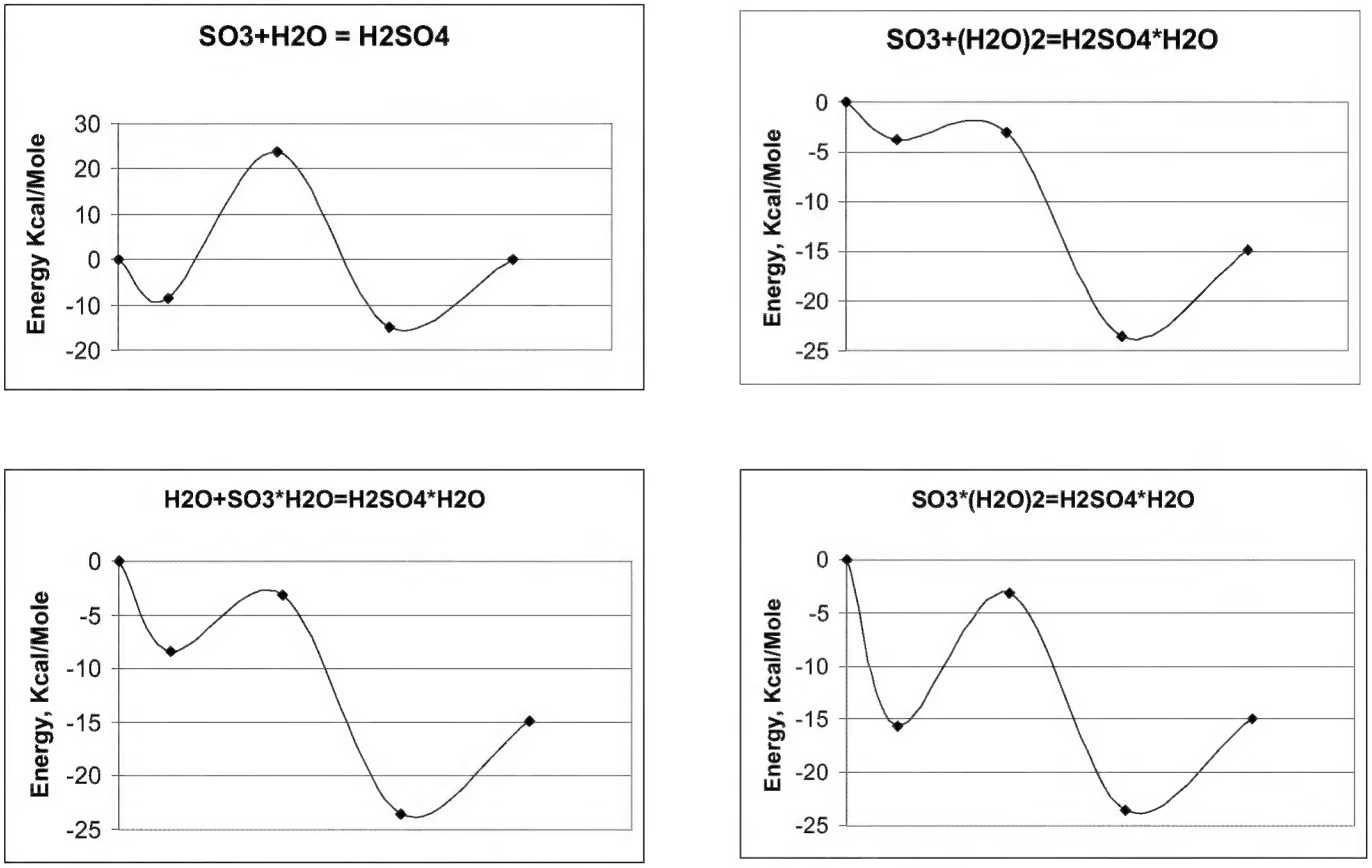

FIGURE 1. The energy profiles for the channels (2…5) of reactions of formation of H_2SO_4

SEMI-EMPIRICAL METHOD

The semi-empirical method uses some simplifications, which allow treating somewhat larger systems and fitting vibrational properties of simple systems to known spectroscopic data (thereby choosing optimal empirical parameters). Semi-empirical methods are especially suitable for organic systems due to the nature of C-H bond. In our investigations of burning problems in supersonic aircraft engine and flows of methane in industrial conditions we have modeled the carbon clusters C_n with n up to 12. It appeared to be two main types of isomers: linear and cyclic, with under n=9 the later having smaller energy. As to gasdynamics consequences it was found that in industrial conditions a number of quasi-staedy states for linear and cyclic clusters exist before the steady state of cluster distribution on size is reached. It is important to take into account for this effect while dealing with technological processes where carbon clusters take part (the primary stage of soot formation process, the initial stage of heavy carbon clusters formation).

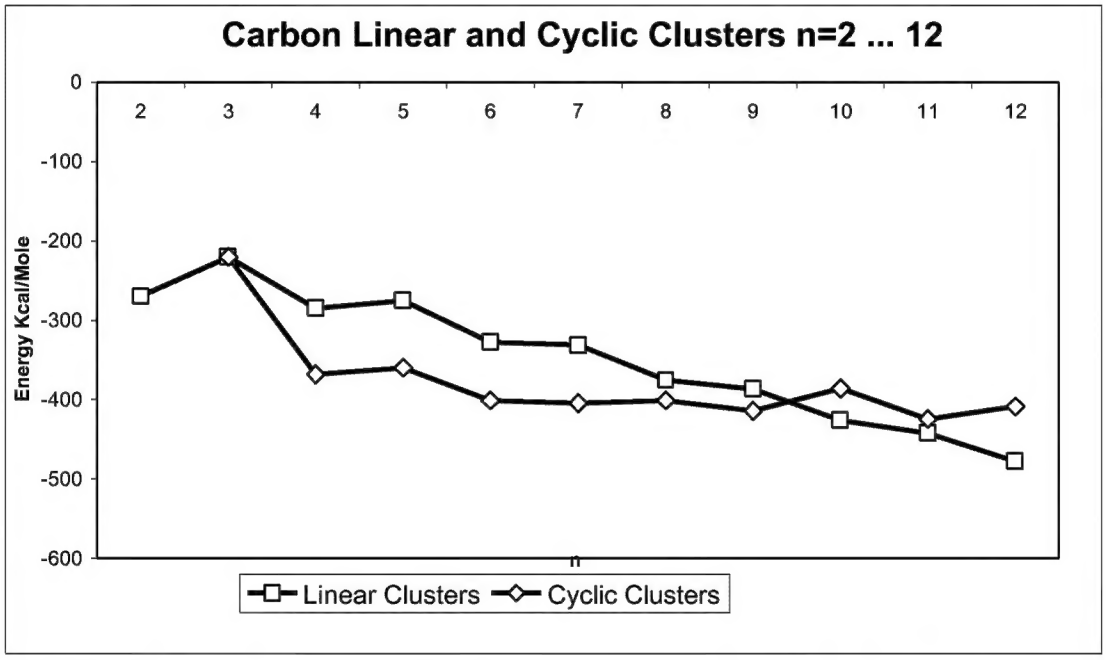

FIGURE 2. The energies of linear and cyclic carbon clusters with n=12, calculated with semi-empirical method.

EMPIRICAL POTENTIAL METHOD

In the third method mentioned - empirical potential method further simplifications are made through the substituting the Schrodinger's equation by Newton's ones and introducing to these equations empirical potential energy already containing potential energy well. Thereby all quantum effects are supposed to be plugged into this potential. These simplifications allow treating rather large systems (up to 10000 molecules in cluster) and what is important to look at the medium region of cluster sizes corresponding to the transition between clusters and continuum limits. With the help of this method we have investigated large water (up to 100 molecules in clusters) and large methane (up to 100 molecules in clusters) systems [5-6]. It should be mentioned that within the frame of this method for water and methane clusters the dissociation energy obeys the linear dependence on n - number of molecules. This allows us to extrapolate its behavior to at least next few n. We can also approximately treat the normal modes problem within the frame of solid state physics and calculate the reaction rate constant for the reaction of adding of one molecule to the large cluster. Thereby taking into account the opposite reaction of dissociation with the help of gasdynamics we can find the dynamical distribution of small droplets and aerosols in the flow under consideration.

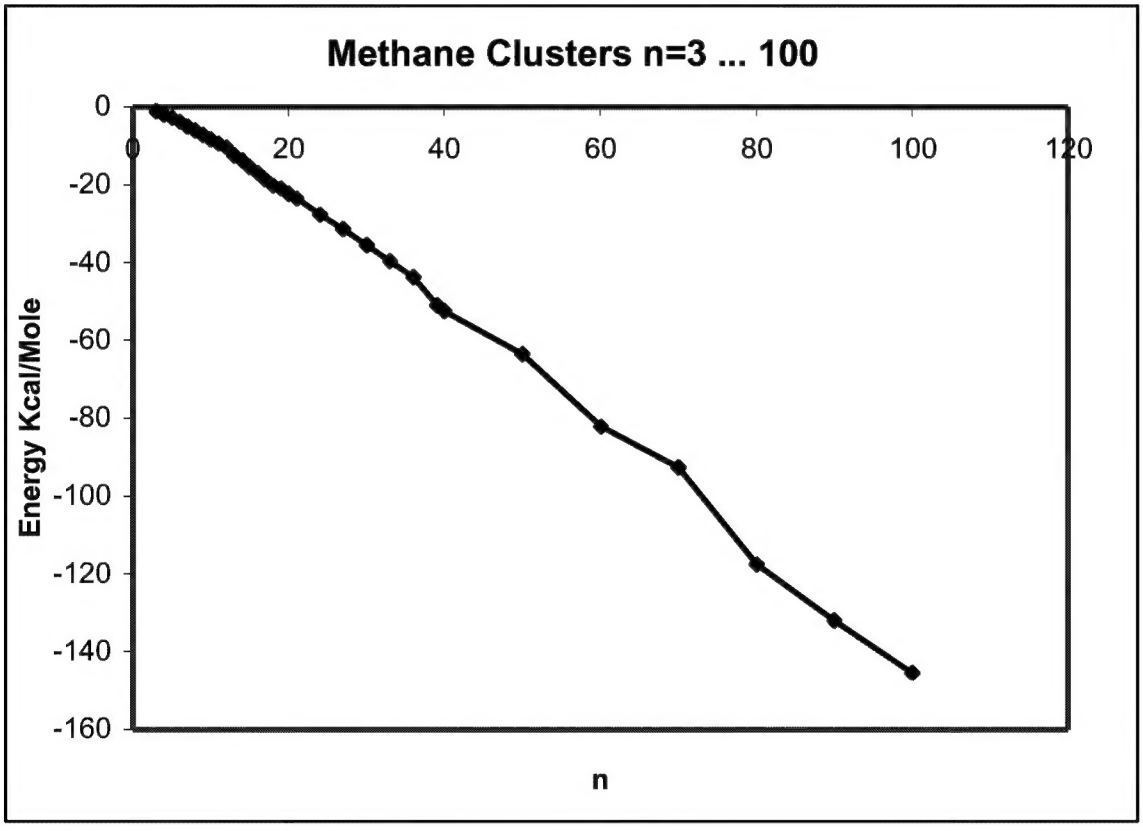

FIGURE 3. The energies of methane clusters with 3=n=21, calculated with empirical potential method.

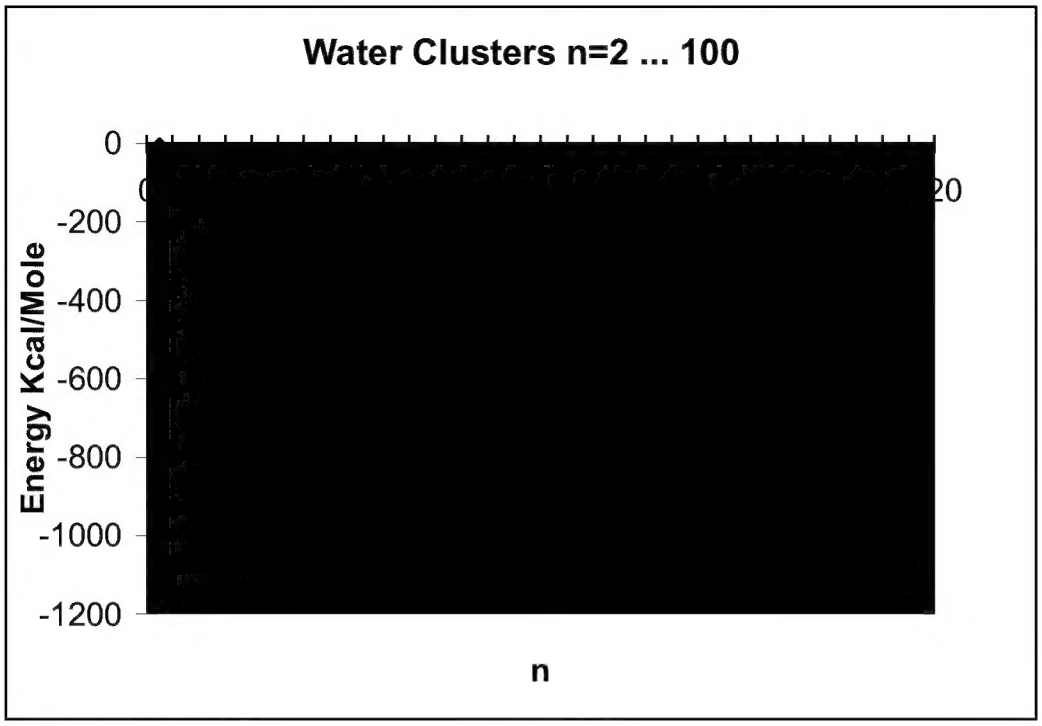

FIGURE 4. The energies of water clusters with 2=n=21, calculated with empirical potential method.

All the calculations ere made with the program Tinker [6].

CONCLUSIONS

Summarizing up it is worthwhile to point out that in each particular problem under consideration the choice of method for calculating of clusters is dictated by the characteristic sizes of clusters as well as how detailed information do we want to get. For large clusters the linear dependence of dissociation energy of n makes it valid the application of empirical potential methods and molecular dynamics. For small clusters both ab-initio and semi empirical methods can be applied with the former giving as a rule more precise results and allowing even further corrections with the help of Moller-Plesset perturbation theory. For organic containing systems semi-empirical methods are the most convenient.

ACKNOWLEDGMENTS

I would like to thank for the valuable help Prof.Egorov B. V. and Prof. Tchougreeff A. L.

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